Applied Catalysis B: Environmental 152–153 (2014) 28–37

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Novel sulfation effect on low-temperature activity enhancement of CeO_2-added Sb-V_2O_5/TiO_2 catalyst for NH_3-SCR

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ARTICLE INFO

Article history:
Received 6 November 2013
Received in revised form 3 January 2014
Accepted 12 January 2014
Available online 22 January 2014

Keywords:
CeO_2/TiO_2
Cerium(III) sulfate
Beneficial sulfation
NH_3-SCR
NO_x conversion

ABSTRACT

Sulfur dioxide (SO_2) is considered as a poisoning gas for NH_3-SCR catalysts under real time conditions. However, it has revealed an obvious beneficial effect on the activity of CeO_2 containing catalysts. Hereby we report the applied research in sulfation effect on low-temperature activity enhancement of CeO_2-modified, Sb_2O_3–V_2O_5–TiO_2 catalyst system pretreated with SO_2 under oxidizing conditions at different temperatures for 2 h. We have elucidated the real insights via nature-property relationships of the species formed at various SO_2 pretreatment temperatures (T = 300, 400 and 500 °C) with the help of advanced characterization techniques such as X-ray diffraction (XRD), temperature programmed reaction (NH_3-TPD, NO-TPD and H_2-TPR), BET surface area, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM–EDS) and X-ray photoelectron spectroscopy (XPS). Our results indicated that SO_2 pre-treatment at 500 °C led to the maximum favorable sulfation with cerium(III) sulfate as the major surface species.

1. Introduction

The oxides of nitrogen (NO_x) have been a major source of air pollution. The major sources of NO_x are the combustion of fossil fuels, particularly petroleum and its products in vehicle engines as well as coke in thermal power plants [1–3]. NO_x (x = 1, 2) emissions can cause adverse effects to the environment and human health through increasing ground level ozone by reacting with volatile organic compounds (VOC) and particulate matter. The reduction of NO_x emissions by NH_3-SCR (selective catalytic reduction) is one of the most efficient technologies used for eliminating NO_x from stationary power plants and diesel engines exhaust.

The well-known commercial catalysts such as V_2O_5–WO_3 (or MoO_3)/TiO_2 have been widely used for decades [4,5]. The addition of WO_3 and/or MoO_3 to V_2O_5/TiO_2 can increase the activity and stability for NH_3-SCR in the temperature window of 290–420 °C, reduce ammonia oxidation, and greatly increase the poison resistance to alkali and arsenious oxides. Although the vanadia based catalysts have been commercialized for the SCR technology, still there is room for improvement in low-temperature activity under abundant SO_2 conditions. The main problems related to NH_3-SCR catalysts based on vanadia include high activity for SO_2 oxidation to SO_3, formation of N_2O at high temperatures, and toxicity of vanadia. The formed SO_3 can cause additional problems because SO_3 combines with H_2O, and results in NH_3-slip to form ammonium sulfates and H_2SO_4 that lead to pore plugging of the catalysts and corrosion of the equipment at low temperatures (<250 °C) [6–8].

In the past decades, great efforts have been devoted to the improvement of low-temperature sulfur-resistance of V_2O_5 based catalysts for NH_3-SCR [6,9–11]. Such studies reveal that the SO_2 has complicated effect on SCR activity, however deactivating the catalysts at temperatures below 300 °C. Previous investigations by Orsenigo et al. [7] compared effects of sulfation on NO_x reduction and SO_2 oxidation activities, suggesting that the sulfation occurs first on vanadia sites and later on TiO_2 and tungsten sites. The sulfur species formed on the catalyst surface either enhance or reduce catalyst activity depending on their nature and properties [12–14]. It is also reported that the surface sulfate species formed after sulfation strengthened the active BrØnsted acid sites which may increase and stabilize catalyst activity [15].

Recently, ceria (CeO_2) has received considerable attention for NH_3-SCR because of its high oxidation and reduction abilities which promote NO oxidation at low temperatures. Ceria-mixed oxide catalysts, such as Ce–Cu–Ti oxides [16], Mn–Ce/TiO_2 [17,18], CeO_2/TiO_2 [19], $Ce_xTi_{1-x}O_2$ [20], CeO_2–WO_3/TiO_2 [21] and CeO_2–WO_3 [22] have shown excellent NH_3-SCR activity and N_2 selectivity, but poor sulfur tolerance. Chang et al. reported that MnO_x–CeO_2 mixed oxide catalyst showed high resistance to SO_2 with the addition of Sn [23]. This positive effect is most probably due to the formation of more cerium(III) sulfates [24]. However, at temperatures below 300 °C, it still remains a big challenge to develop sulfur-tolerant catalysts for NH_3-SCR.

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http://dx.doi.org/10.1016/j.apcatb.2014.01.017

In our latest studies for NH_3-SCR of NO_x, we have reported ceria-added Sb-V_2O_5/TiO_2 catalyst, which showed high sulfur tolerance at 240 °C [25,26]. The aim of the present work is to investigate the real nature of beneficial sulfate and its role in low-temperature activity enhancement of ceria-added Sb/V_2O_5/TiO_2 catalyst. The as-prepared and sulfated catalysts were characterized by X-ray diffraction (XRD), Temperature programmed desorption/reduction (TPD/R), Brunner–Emmett–Teller surface area (BET-SA), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The current study is considered to be of great importance with regards to its application under severe SO_2 and H_2O conditions.

2. Experimental

2.1. Catalyst preparation

The CeO_2 modified, Sb-V_2O_5/TiO_2 catalysts were prepared by incipient wetness co-impregnation and deposition–precipitation methods, as discussed in our previous report [25]. The synthesized sample after calcination was denoted as "as-prep.". For sulfated catalysts, the as-prepared samples were treated with SO_2 (500 ppm) and O_2 (3%) with balance N_2 for 2 h at various (300, 400 and 500 °C) temperatures. The samples were then labeled as S300, S400 and S500, respectively.

2.2. Physico-chemical characterization

The BET (Brunauer–Emmett–Teller) surface area was measured from the N_2 adsorption and desorption isotherms at −196 °C using the ASAP-2010 (Micromeritics) analyzer. The catalysts were analyzed by powder X-ray diffraction (Bruker) and the spectra were recorded using Ni-filtered Cu K_α radiation operated at 40 kV and 40 mA. Due to unknown level of homogeneity of the sulfate species formed in pretreated catalysts, the samples were rotated at a rotation speed of 15 rpm during analysis. NH_3 and NO TPD experiments were carried out using the AutoChem II-2920 (Micromeritics) chemisorptions analyzer. For each experiment, 100 mg of catalyst was placed in a U-shaped quartz cell and preconditioned at 120 °C in He gas at a flow rate of 50 mL min^{-1}. Accordingly, 1% NH_3 and 1% NO under He balance were used as adsorption media (50 mL min^{-1} flow) at 50 °C for 60 min. Furthermore, the samples were heated to 100 °C, purged with He gas to remove the physically adsorbed gases, and cooled down to the starting point of 50 °C. Afterwards, the TPD run was conducted from 50 to 550 °C at a heating rate of 10 °C min^{-1}. Simultaneously, TPD–mass spectra were analyzed by HPR-20 QIC (Quartz Inert Capillary) (HIDEN analytical) real time gas analyzer (RGA) for multiple species of molecular weight up to 300 amu. The quantity of NH_3 (NH_3-TPD) was calculated by measuring the average area of 5 consecutive 1 cc volume pulse injections (similar areas) of 5% NH_3/He gas. H_2-TPR experiments were carried out by heating the catalysts (each 100 mg) at a linear heating rate of 10 °C min^{-1} between 50 and 900 °C with 10% H_2/Ar at a constant flow rate of 50 mL min^{-1}. XPS studies were carried out by using PHI 5800 ESCA system, employing a non-monochromatic Al K_α (1486.6 eV) source. The binding energies were referenced to the C 1s line at 284.6 eV from adventitious carbon. Scanning electron microscopy (SEM) images were taken by Hitachi S-4200 FE-SEM equipped with EDS (energy dispersive X-ray spectroscopy) at an acceleration voltage of 15 kV.

2.3. Activity measurements

The SCR of NO_x ($NO + NO_2$) over the synthesized catalytic materials was evaluated by using ammonia as a reductant. The conversion of NO_x was determined over a down flow fixed-bed reactor system.

Table 1
Physical properties of as-prepared and sulfate samples at different temperatures.

Sample name	BET surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
As-prep.	54.4	20.0	0.28
S300	57.8	18.1	0.27
S400	62.0	17.4	0.29
S500	58.7	16.3	0.26

The quartz reactor (1 cm o.d. and 50 cm length) was placed vertically in a tubular furnace connected to a temperature controller indicator. To minimize the mass transfer limitations, the catalyst was sieved with 40–50 mesh size and then charged into the quartz reactor using quartz wool. Prior to each experiment, about 0.5 mL catalyst was pre-treated by a mixture of 3% O_2 and N_2 flowing at 500 °C for 1 h. A reaction stream consisting of 800 ppm NO_x, 800 ppm NH_3, 3 vol.% O_2, 6 vol.% H_2O, 500 ppm SO_2 and N_2 balance was fed into the reactor system through mass flow controllers with a total flow rate of 500 mL min^{-1} and at a space velocity of 60,000 h^{-1}. Water vapor was produced by passing N_2 gas through a heated glass wash bottle containing de-ionized water. Catalytic activity measurements were performed in a top-down pattern over a low temperature range (350–175 °C). Additionally, the stability tests for as-prepared and sulfated catalysts were carried out at 225 °C for 5 h. For each stability test, in case of sulfation pretreatment involved, the temperature was decreased directly from the sulfation temperature (in the presence of 3% O_2 and N_2 balance) to 225 °C. The effluent from the reactor was analyzed by an online NDIR Fuji NO and SO_2 analyzer. NO_2 amount was determined by converting NO_2 into NO with Gas converter series CG-2M analyzer. The percentage conversion of NO_x was calculated by using the formula given below.

$$NO_x \text{ conversion} = \left(\frac{[NO_x]_{in} - [NO_x]_{out}}{[NO_x]_{in}}\right) \times 100 \quad (1)$$

3. Results and discussion

3.1. Catalyst characterization

3.1.1. BET surface area

Physical properties of a catalyst such as, surface area, pore diameter and pore volume are very important to determine the adsorption–desorption phenomena of gases onto its surface. Table 1 compares these physical measures for fresh and sulfated catalysts at different temperatures. Interestingly, all the sulfated catalysts showed an increment in the BET surface area after sulfation pretreatment. This gives a clue about the formed sulfates to be amorphous in nature. Moreover, pore diameter of the catalysts was reduced after sulfation, especially in case of the sample treated at 500 °C. Since the amount of SO_2 used during pretreatment also increased with increasing temperature, these sulfates seem to enter the pores of the catalysts, thereby decreasing both the pore diameters and pore volumes of the sulfated catalysts.

3.1.2. X-ray diffraction (XRD) studies

Fig. 1 illustrates the XRD patterns for the fresh and sulfated catalysts along with the possible cerium sulfates. The as-prepared catalyst exhibited characteristic CeO_2 [PDF-ICDD 81-0792] and TiO_2-anatase [PDF-ICDD 86-1157] peaks. The peaks corresponding to Sb_2O_3 and V_2O_5, could not be detected possibly because of their nominal addition and well-dispersion of the oxides. Furthermore, no CeO_2 peak could be observed in any of the sulfated catalysts, which could suggest preferential sulfation of ceria lessening its crystallinity [24]. It is also important to note that none

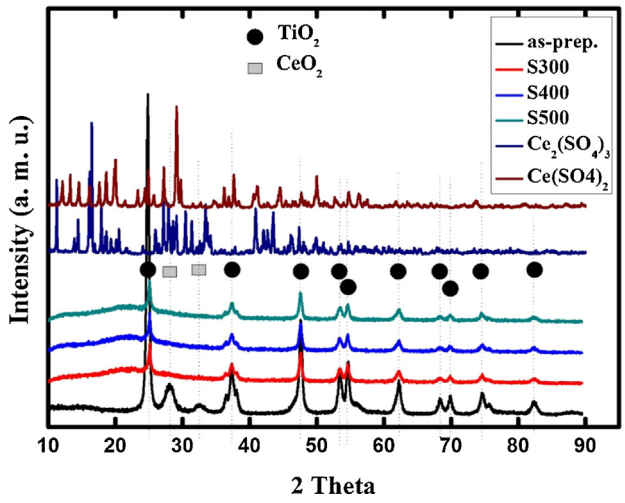

Fig. 1. XRD patterns of the catalysts, as-prepared and sulfated at different temperatures along with commercial $Ce_2(SO_4)_3$, and $Ce(SO_4)_2$.

of the possible cerium sulfates could be observed in the sulfated samples. This implies that either the formed sulfates were too low in the quantity to be detected by XRD, or amorphous in nature.

3.1.3. SEM and EDS analyses

In order to determine their morphology, all the fresh and sulfated samples were characterized by FE-SEM (Field emission scanning electron microscopy). The resultant micrographs of the studied catalysts have been demonstrated in Fig. 2. However, the images could not present any obvious difference among the fresh and sulfated catalysts at various temperatures. Therefore energy dispersive spectroscopy (EDS) of the samples was carried out in order to detect the amount of sulfur in sulfated catalysts, and the resultant peak intensities have been presented in Fig. 3. In case of sulfated catalysts, an additional peak of sulfur was observed. Moreover, similar to our SO_2 usage data during sulfation pretreatment, more sulfur amount was detected in S500 sample (not shown here), which confirms the formation of relatively more sulfate species than in the samples sulfated at low temperatures (S300 and S400).

3.2. Activity measurement

Effect of sulfation pretreatment in the oxidizing environment on low-temperature activity of the catalyst was observed in terms of NO_x conversion over a temperature range of 350–175 °C (Fig. 4a). All the samples showed 100% NO_x conversion (except 97% for S300) at temperatures ≥250 °C due to active redox species such as V_2O_5 and CeO_2 [11,27]. However below 250 °C, the activity declined most probably due to the formation of both low-temperature sulfate species as well as ammonium bisulfate (ABS). Among all the samples, the highest activity in low-temperature range was shown by S500 catalyst, which suggests that the sulfates formed at 500 °C are the most favorable for NH_3-SCR of NO_x. Contrastingly, the activity measurements at low temperatures (≤250 °C) for other three samples could not illustrate a clear difference, possibly due to lower resistance against SO_2-poisoning. However SO_2 usage data, (shown in Fig. 4b), suggests that the tendency of sulfate formation is lower onto the pre-sulfated catalysts at higher temperatures (≥250 °C). This might be due to repulsive interaction between SO_2 and the pre-formed sulfates. The as-prepared catalyst consumed more amount of SO_2 during the course of reaction. This could be due to consumption of SO_2 by catalyst itself for cerium sulfate formation, as well as to form the ammonium sulfates. However, the formed initial sulfate species on the as-prepared catalysts seemed undamaging for the NH_3-SCR. So, the as-prepared catalyst showed slightly higher activity than that of S300 catalyst at low temperatures. While the sulfate species on as-prepared catalyst were formed at a temperature far less than 500 °C. As a consequence, the as-prepared catalyst showed lower activity than S500, which suggests that the sulfates formed at 500 °C are the most favorable for NH_3-SCR.

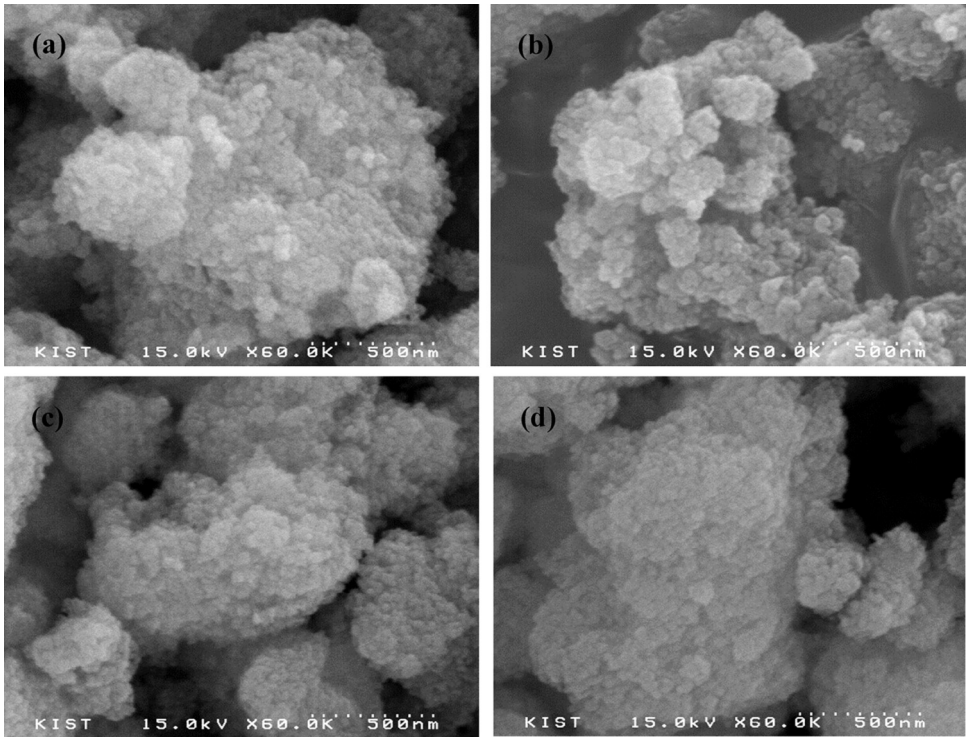

Fig. 2. SEM images of the catalysts, as-prepared and sulfated at different temperatures: as-prep., (b) S300, (c) S400, and (d) S500.

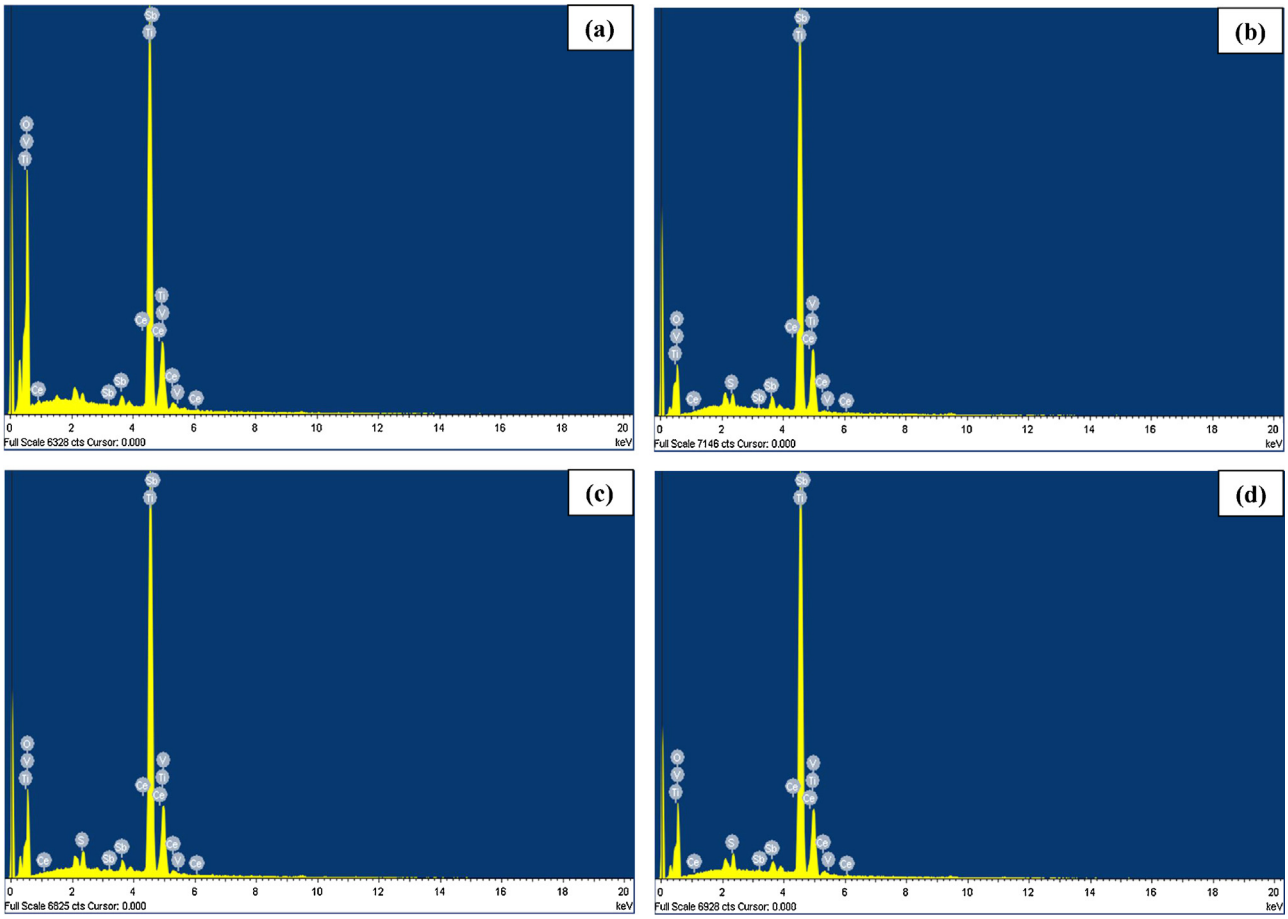

Fig. 3. Elemental peak intensities from energy dispersive spectroscopy (EDS): as-prep., (b) S300, (c) S400, and (d) S500.

In order to have a closer look on effect of sulfation pretreatment at low-temperature activity, all the catalysts were subjected to stability tests at 225 °C for 5 h. The as-prepared catalyst (without any sulfation treatment), showed 83% conversion which underwent an ordinary change in its activity (≈80% conversion) after the total runtime of 5 h. The sample pretreated at 300 °C for 2 h (S300) started with a slightly higher activity (≈85% conversion) however suffered from deactivation after 5 h (≈75% conversion). This deactivation might be due to less favorable, low temperature sulfate species formed during sulfation pretreatment at 300 °C. Yang et al. have reported similar results for CeO_2 catalyst, where $SO_2 + O_2$ pretreated samples at 300 °C for 8 h showed poor activity as compared to that of a fresh sample at low temperatures under SO2 conditions [27]. The catalyst treated at next higher temperature i.e., 400 °C (S400) showed an improved catalytic activity initially (≈88% conversion) when compared to as-prepared and S300 catalysts. However, its activity was also declined, and reached a value closer to that of as-prepared sample after 5 h run (81%). The activity shown by S500 C was the highest and most sustainable among all. It showed a NO_x conversion of ≈94%, and could retain its activity around 90% after 5 h. The above results have suggested a positive impact of sulfation pretreatment under oxidizing conditions on the Ce-modified Sb-V_2O_5/TiO_2 catalyst. All the pretreated samples, when compared to as-prepared catalysts, have shown an improved activity at the start. However, the pretreatment temperature has been proved to be a critical measure for long-term stability of the catalyst at low temperature.

Fig. 5b represents the comparison for amount of SO_2 used (ppm) by each catalyst during and after sulfation pretreatment. It can be clearly seen that a lot of SO_2 was used during sulfation of the catalyst at highest temperature (500 °C) throughout pretreatment duration. This SO_2 used is supposed to form beneficial cerium sulfate species most probably on the surface of the catalyst, as discussed later. However, as the pretreatment temperature was decreased, only a small amount of SO_2 was consumed for the purpose. This suggests that the sulfation temperature is an important factor for the formation of surface sulfate species on the catalyst. The sulfation under given oxidizing environment seems to be kinetically favorable at higher temperatures.

In order to confirm that the origin of beneficial sulfation was from CeO_2 component of the catalyst system, a Sb-V_2O_5/TiO_2 catalyst (without CeO_2 addition) [28] was evaluated for its catalytic performance with and without sulfation treatment. The resultant activity graphs are shown in Fig. 6a. It can be clearly seen that, despite similar composition, no activity improvement could be observed for catalyst without CeO_2. Oppositely, the activity was decreased over time after sulfation treatment, most probably due to formation of ammonium bisulfate (ABS) species at such a lower temperature [6,29]. From SO_2 usage data presented in Fig. 6b, it can be observed that a lot of SO_2 was used with the passage of time, especially for the sulfated sample which seemed to be poisoned by sulfation.

The effect of sulfation on NH_3-SCR activity of the catalysts has been a matter of debate for a decade or two. Based on our literature review, the promotional effect of SO_2 in the presence of H_2O on V_2O_5/TiO_2 catalysts was first reported by Amiridis et al. [11]. They found that during the SCR reaction of NO by NH_3, the turnover frequency at low surface vanadia coverage was enhanced with the presence of SO_2 in the reaction gas stream, without any maximum at vanadia loadings exceeding half a monolayer. As a conclusion,

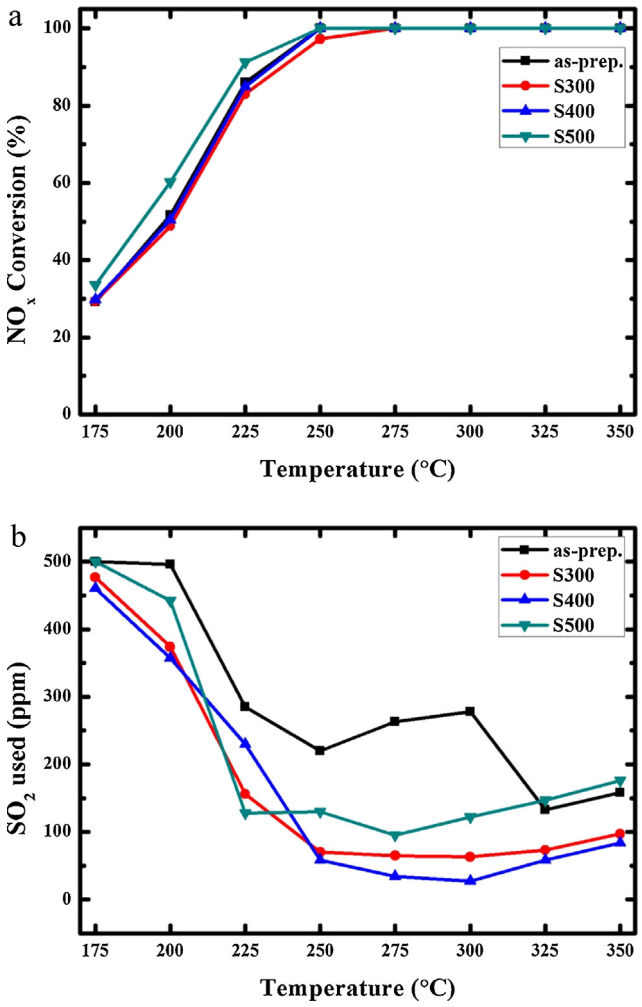

Fig. 4. Effect of sulfation pretreatment temperature on the activity at low temperatures: (a) NO_x conversion and (b) amount of SO_2 used (reaction conditions: $[NO_x] = [NH_3] = 800$ ppm, $[O_2] = 3$ vol.%, $H_2O = 6$ vol.%, $SO_2 = 500$ ppm, N_2 balance, GHSV = 60,000 h^{-1}).

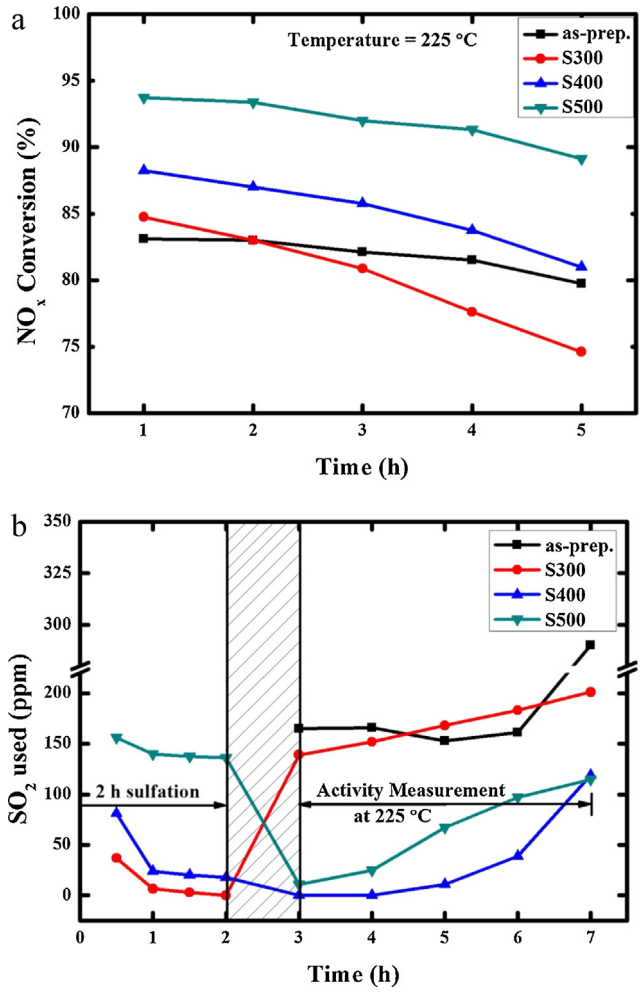

Fig. 5. Effect of sulfation pretreatment temperature on stability of the catalysts at 225 °C: (a) NO_x conversion and (b) amount of SO_2 used (reaction conditions: same as given in Fig. 4).

they ascribed the beneficial effect of SO_2 to strong Brønsted acidic sites by the reaction between H_2O and SO_2, existing in the form of surface sulfates. From our results presented in Fig. 5a, it could be clearly seen that the sulfation at low temperatures (300 and 400 °C) could be detrimental for the catalyst activity. Despite the formation of quite few cerium sulfates, both the catalysts (S300 and S400) showed declined activities at low temperature as compared to that of S500catalyst. While it is important to note that the activity of as-prepared sample remained almost unchanged throughout the activity run of 5 h. Since the as-prepared catalyst used up around 150–170 ppm SO_2 in the first 4 h of run, it can be concluded that the initial sulfation of the catalyst resulted preferably in the formation of Ce-sulfates. On the contrary, the activity curve of S300 catalyst surprisingly followed a steep slope after about 2 h of activity measurement. This suggests another view point that the sulfates formed at low temperatures (<500 °C) might differ in nature from those formed at high temperatures. Therefore, in order to differentiate between them, the sulfate species formed at 300 and 500 °C will be termed from now onwards as 'low-temperature sulfates' and 'high-temperature sulfates', respectively. Contrastingly, the sulfates formed at 400 °C were thought to have mixed nature of low- as well as high-temperature sulfates, as discussed in details later on.

Xie et al. [30] reported the promotional effect of SO_2 on SCR activity of CuO/Al_2O_3 catalyst sorbent due to the formation of sulfate species. However, they could find out that the sulfates formed at temperatures below 300 °C were not active enough for NH_3-SCR of NO. We have also noticed a similar trend for our catalyst, where the sample pretreated at 300 °C underwent deactivation badly. The beneficial effect of sulfation over CeO_2 for NH_3-SCR of NO_x over a wide temperature range (275–525 °C) was reported first by Gu et al. [24]. Based on our results, it is obvious that the temperature of sulfation should be higher than 400 °C in order to promote low temperature activity by the formation of beneficial surface cerium sulfates.

3.3. Supportive characterization

3.3.1. NH_3-TPD

The amount and strength of acidic sites present on the surface of a catalyst can be determined through adsorption/desorption studies of a basic gas i.e., NH_3. The samples were heated from 50 to 550 °C in order to find out the NH_3-desorption behavior for the catalysts, and the curves obtained are depicted in Fig. 7. All the catalysts showed two peaks: first one in the range around 100–300 °C, and the second one in the range around 300–450 °C. The as-prepared (fresh) catalyst showed lowest amount of acidic sites as compared to sulfated catalysts. Yang et al. [27] and Gao et al. [31] also reported that the number of acidic sites is increased upon sulfation. The amount and strength of acidic sites on S300 sample were much higher than those found in S400 and S500.

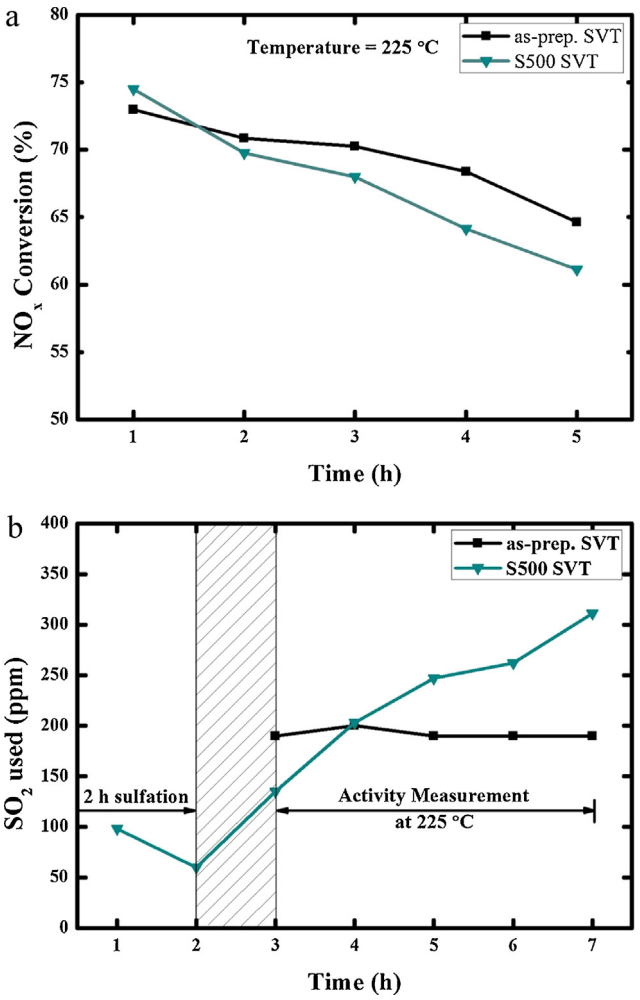

Fig. 6. Effect of sulfation pretreatment on stability of the catalyst Sb–V_2O_5/TiO_2 (without CeO_2) at 225 °C: (a) NO_x conversion and (b) amount of SO_2 used (reaction conditions: same as given in Fig. 4).

This strong and excessive adsorption of NH_3 could inhibit the catalyst performance at lower temperatures [32]. Nova et al. could propose a number of reasons for this NH_3-inhibition effect. Firstly the excess ammonia might adsorb onto the pre-adsorbed NH_3, without any activation and interaction with gaseous NO. Secondly

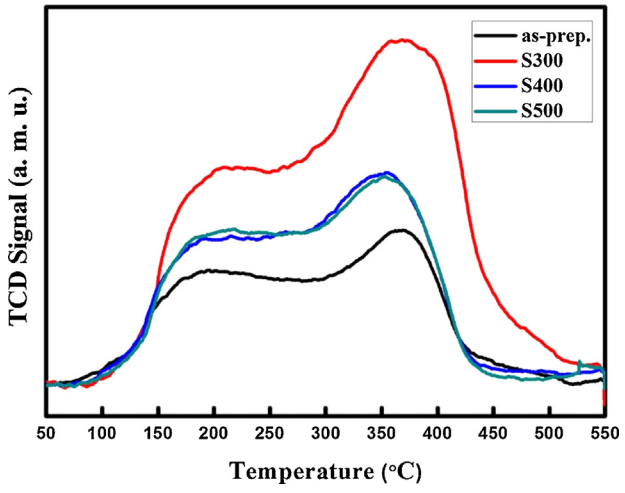

Fig. 7. NH_3-TPD profiles of the catalysts, as-prepared and sulfated at different temperatures.

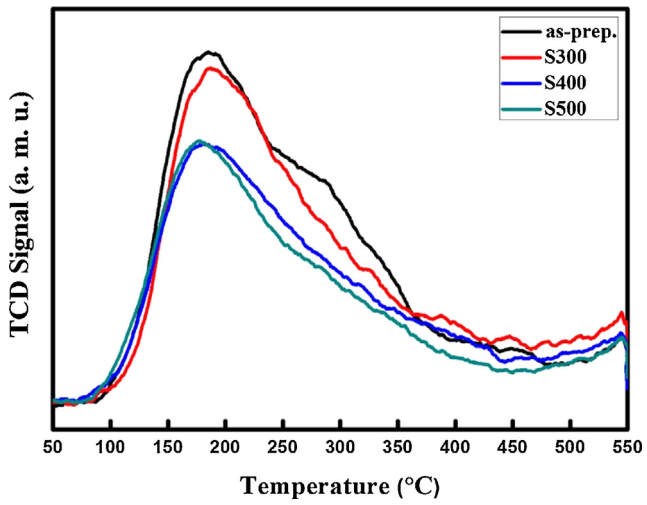

Fig. 8. NO-TPD curves for the catalysts, as-prepared and sulfated at different temperatures.

beneficial, competitive NO adsorption and activation, reported for active oxide-based systems for NH_3-SCR [4], could be prohibited by excess NH_3 adsorption. Thirdly quite closer to our catalyst system, NH_3 adsorbed onto an acidic site in the vicinity of redox specie could exacerbate its function either by blocking it or through interaction between their electrons. Both S400 and S500 could barely show a difference in strength of their acidic sites. By having a closer look on mass spectra (Fig. S1a and S1b), S300 sample showed the highest NH_3 desorption, followed by S400 and S500 respectively. Interestingly, S300 catalyst also showed highest NO_x formation by NH_3 oxidation. Based on our activity results, the sulfates formed on S300 catalyst seemed to be inactive for NH_3 activation to reduce NO. Comparatively, S400 catalyst showed intermediate activity between those of S300 and S500 catalysts. Therefore, it suggests that the nature of sulfates species formed on S400 catalyst is a mixture of those present in S300 and S500 samples. The sulfate species formed on S500 could be the most active species for NH_3 activation, showing improved and sustainable NO_x conversion.

3.3.2. NO-TPD

In order to compare the NO adsorption behavior of as-prepared and the sulfated catalysts, NO-TPD was carried out; and the resultant patterns have been presented in Fig. 8. Only as-prepared catalyst could show two peaks: first, large one at 187 °C and second, small neck at 290 °C. The first peak could be assigned to low-strength basic sites which released physisorbed NO upon heating. The second peak at higher temperature might show the chemisorbed NO, released from the fresh CeO_2 sites (based on its acid-base properties). Contrastingly, all the sulfated samples showed only single desorption peak at low temperatures with comparatively smaller area. This is an indication of increased acidity of the catalysts after being sulfated. Moreover, the amounts of NO desorbed were variables among the three samples sulfated at different temperatures. This might support the view point that the sulfate species formed at different pretreatment temperatures were dissimilar in their nature. As compared to fresh sample, S300 showed quite low NO adsorption [27]. However, highest NO desorption was observed on S300 sample among the catalysts sulfated at different temperatures (Fig. S2). Both the S400 and S500 catalyst samples showed more or less same NO desorption peak, whereas slightly higher amount of NO desorption was detected for S500 sample than that on S400 at low temperatures (150–275 °C). This could be another reason for higher activity shown by S500 sample than the other sulfated samples.

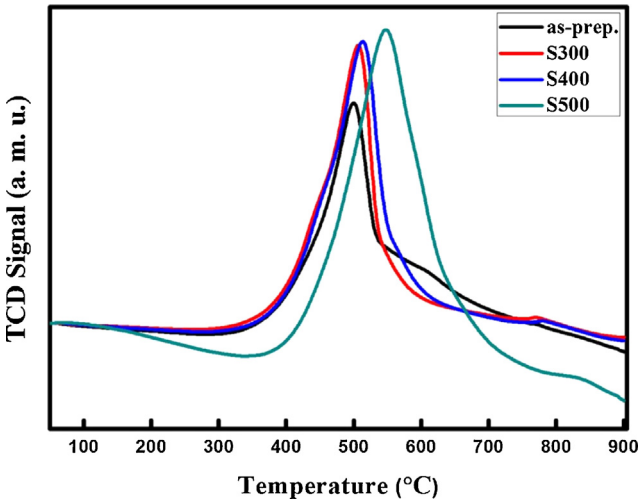

Fig. 9. H_2-TPR profiles of the catalysts, as-prepared and sulfated at different temperatures.

3.3.3. H_2-TPR

The availability and amount of reducible species present on fresh and sulfated catalysts were determined through H_2-TPR. The curves obtained from as-prep., S300, S400 and S500 are illustrated in Fig. 9. All the samples showed two distinct peaks, a large area peak in the range of 300 to 700 °C and a small area peak at higher temperatures around 700 to 900 °C. The low-temperature peaks could arise from reduction of the surface species such as Sb^{5+}, V^{5+}, Ce^{4+} and the sulfates [25]. The as-prepared catalyst showed comparatively smaller reduction peak, and slightly at lower T_{max} (maximum peak reduction temperature) than those of the sulfated samples. This mainly included reduction of Sb^{5+} to Sb^{+3}, V^{5+} to V^{3+}, and Ce^{4+} to Ce^{3+}. Their respective mass spectra data for reduction of oxide species has been presented in Fig. 10. On the other hand, the additional peak area of the sulfated catalysts could arise mainly from the sulfates after SO_2 pretreatment. The H_2O, SO_2 and O_2 mass spectra were detected (Fig. 10a, b and c respectively), which can be assigned to reduction of the oxide species to H_2O, and the decomposition of sulfate species essentially to SO_2 and O_2. Interestingly, the T_{max} of sulfated catalysts were different from one another, and shifted towards right with increase of sulfation temperature. Again, this gives an indication that the sulfates formed at various temperatures are dissimilar in their nature. The samples pretreated at 300 and 400 °C showed a closer T_{max} (around 512 °C), whereas sample pretreated at 500 °C showed a peak maximum at around 551 °C. This difference in peak maxima confirms that the sulfates formed at higher temperatures are different in nature compared to the low-temperature sulfates. According to the literature data, the sulfate species could be reduced at high temperatures [33,34]. Similarly, the sulfated samples showed broad peaks with more consumption of H_2 as compared to as-prepared catalyst. During sulfation process, the sulfated species formed on the ceria are more predominated than the other vanadia, antimony and titania species. It could be due to the higher affinity of ceria with SO_2. In addition, the beneficial sulfation effect was observed in Ce-added catalysts only, as reported previously [25]. In our results we found that the reduction temperatures of S500 samples are higher than those of S400 and S300 catalysts. Simultaneously, the H_2O, SO_2 and O_2 mass spectra (Fig. 10a, b and c) confirm their evolution at higher temperatures on S500 catalyst as compared to S400 and S300. Comparing with their decomposition temperatures provided in literature [35,36], these results suggest that the formed sulfate species on S500 and S300 catalysts correspond to Ce(III) sulfate and Ce(IV) sulfates, respectively. On the other hand, the sulfate species

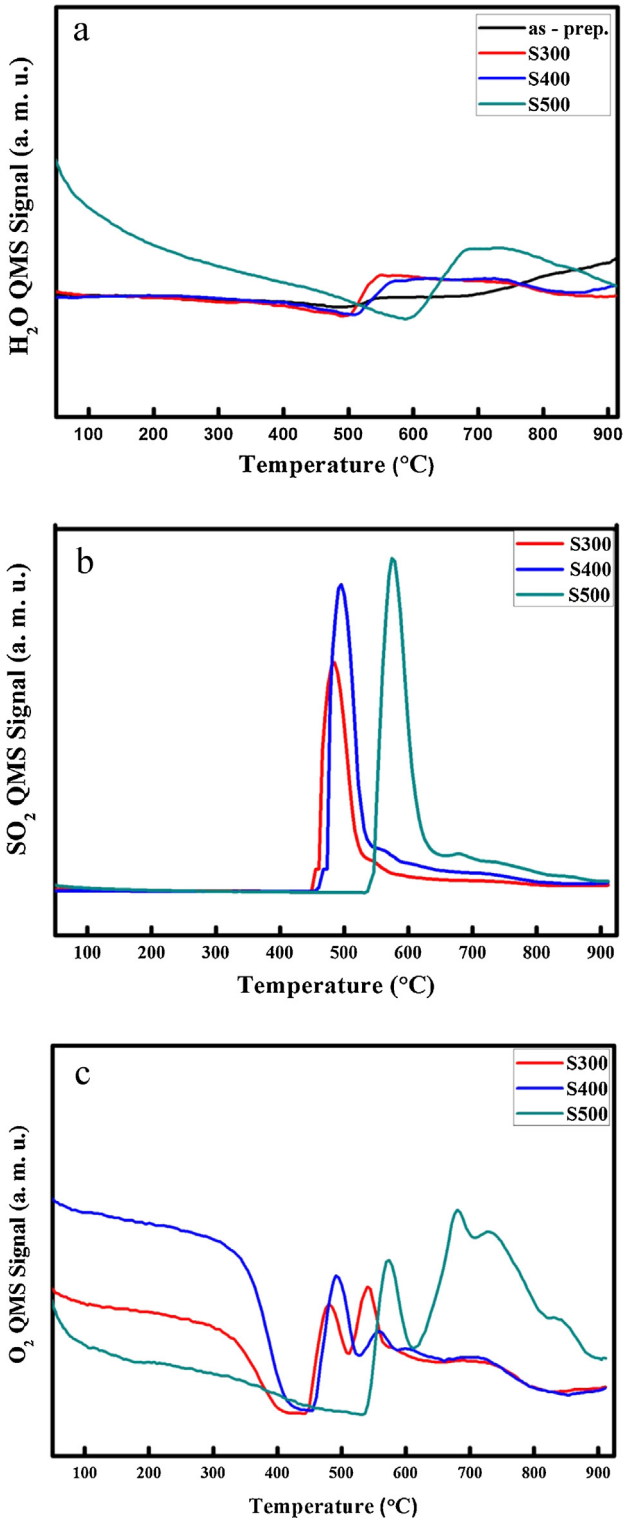

Fig. 10. Mass spectra of H_2-TPR for the catalysts, as-prepared and sulfated at different temperatures: (a) H_2O, (b) SO_2, and (c) O_2 signals.

formed on S400 catalysts contain mixture of Ce(IV) and Ce(III) sulfate species. Moreover, the reduction peak area of S500 catalyst was larger than those pretreated at lower temperatures, indicating higher amounts of sulfates species present on its surface. This observation is in line with SO_2 usage data during SO_2 pretreatment. The second small peak observed at temperatures higher than 700 °C for all the catalysts could be assigned to the reduction of bulk ceria

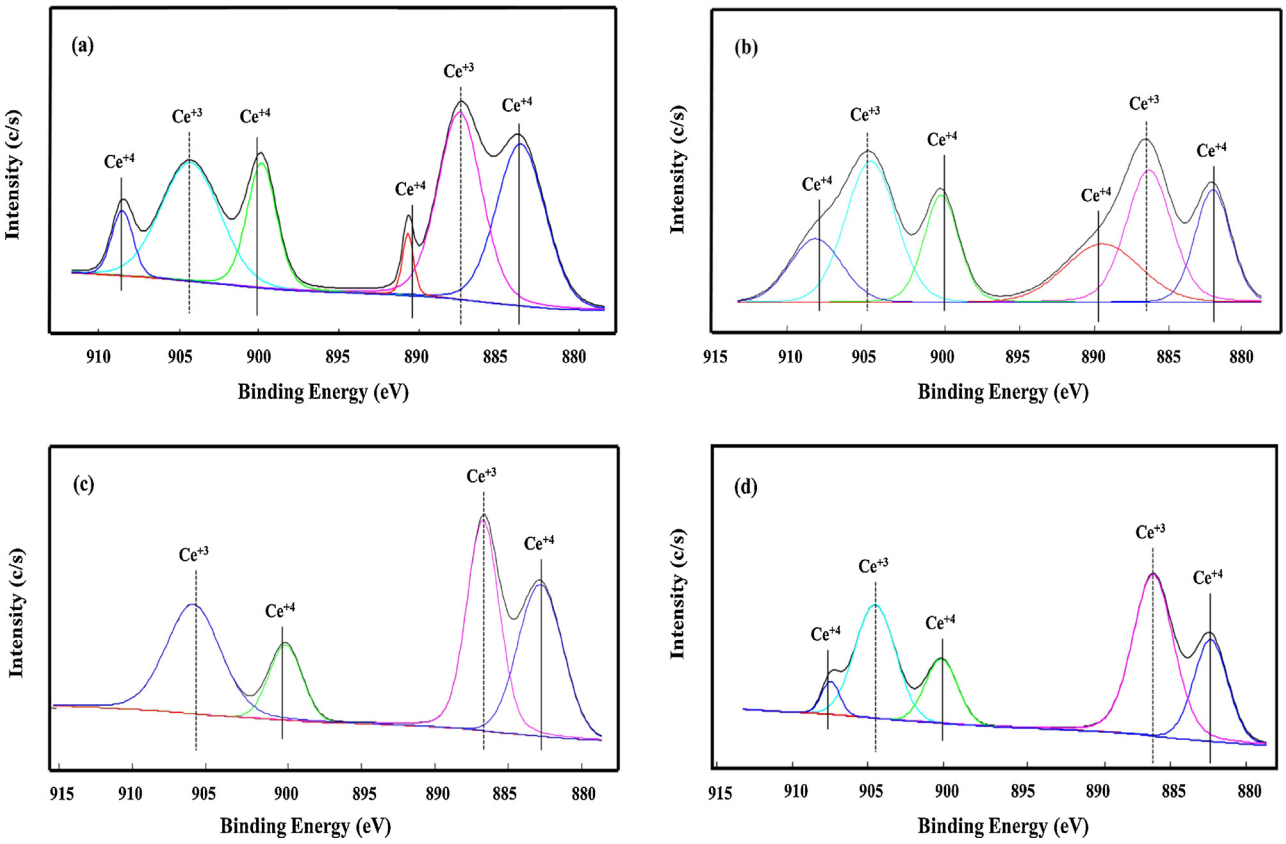

Fig. 11. XPS spectra of Ce 3d for the catalysts, as-prepared and sulfated at different temperatures: (a) as-prep., (b) S300, (c) S400, and (d) S500.

which was readily available after reduction of the surface sulfate species.

3.3.4. XPS studies

The XPS studies were carried out on all the fresh and sulfated catalysts in order to know surface atomic concentrations, and ratios of their different oxidation states. The curves from XPS are depicted in Figs. 11–13, whereas surface elemental compositions have been presented in Table 2. Fig. 11 shows the Ce peak fit for as-prepared, S300, S400 and S500 catalyst samples. The as-prepared catalyst consisted of a balanced Ce^{3+} and Ce^{4+} compositions that provided with reasonably higher activity at temperature as low as 225 °C [37]. However when the sulfation was carried out at 300 °C, the amount of Ce^{4+} species was increased compared to the as-prepared sample. This increase in Ce^{4+} species might be due to the formation of Ce(IV) sulfate species on its surface. On the other hand, both S400 and S500 samples showed an increase in Ce^{3+} content, with S500 having higher content. This increased Ce^{3+} concentrations in these samples after sulfation can be related to the formation of Ce(III) sulfate species. Therefore, it can be concluded that the cerium sulfate species formed at different pretreatment temperatures are unlike in their nature. Moreover, the amounts of Ce(III) species are more abundant on the surface of S500 catalyst. Based on our activity results, it could be inferred that Ce(III) sulfate species are highly active for NH_3-SCR of NO_x, and are formed in abundance at high temperature (500 °C) pretreated catalysts. These Ce(III) species (in the form of sulfate) could favor NH_3 adsorption and activation, whereas the rest of Ce^{4+} species (in the form CeO_2) could adsorb sufficient amount of NO for its reduction with ammonia to N_2 and H_2O. Secondly, increased oxygen vacancies in the sulfated samples due to reduction of Ce^{4+} to Ce^{3+} could also help in oxygen migration from bulk and adsorption from the gaseous phase. This redox cycle is believed to be the reason for increased activity by fast SCR reaction at low temperatures in Ce-added catalysts [38,39].

Oxygen peak fits for as-prepared and sulfated catalysts are presented in Fig. 12. The peaks were deconvoluted into two: O_α and O_β, as mentioned elsewhere [25]. After being sulfated, the amount of chemisorbed oxygen was increased which can be released during oxidation cycle. Since it could be more easily available to the surface than from the bulk, it could speed up the oxidation step in complete redox reaction. Fig. 13 presents the XPS peak fits for sulfur in the sulfated samples. All the sulfated catalysts exhibited S_{2p} peak in the range of 168.6–169.3 eV binding energy, which is characteristic for S^{6+} oxidation state in sulfate form [40,41]. This confirms the formation of sulfate species onto the sulfated catalysts. Again the amount of sulfur detected (Table 2), increased with increasing sulfation temperature, which proves higher amounts of the surface sulfate species formed.

Based on our characterization and activity results at low temperature (225 °C), catalytic performance of the sulfated samples can be summarized as shown in Fig. 14. Excess ammonia adsorption onto low-temperature sulfated catalysts (Fig. S1a) can inhibit direct contact of gaseous NO with the activated NH_3 and/or blocking of the active redox species. However its activity might be resulted from the reaction between adsorbed (Fig. S2) or gaseous NO and activated NH_3, as it showed highest NO desorption as compared to other sulfated samples. Moreover, since all CeO_2 could not be sulfated at low temperature by sulfation pretreatment, NO reduction could also occur by the reaction between gaseous NO and NH_3 activated by CeO_2 and/or V_2O_5 species. In case of high-temperature sulfated sample, sufficiently high amount of NH_3 and NO adsorption along with more reducible species resulted in highest achievable activity among fresh and other sulfated catalysts.

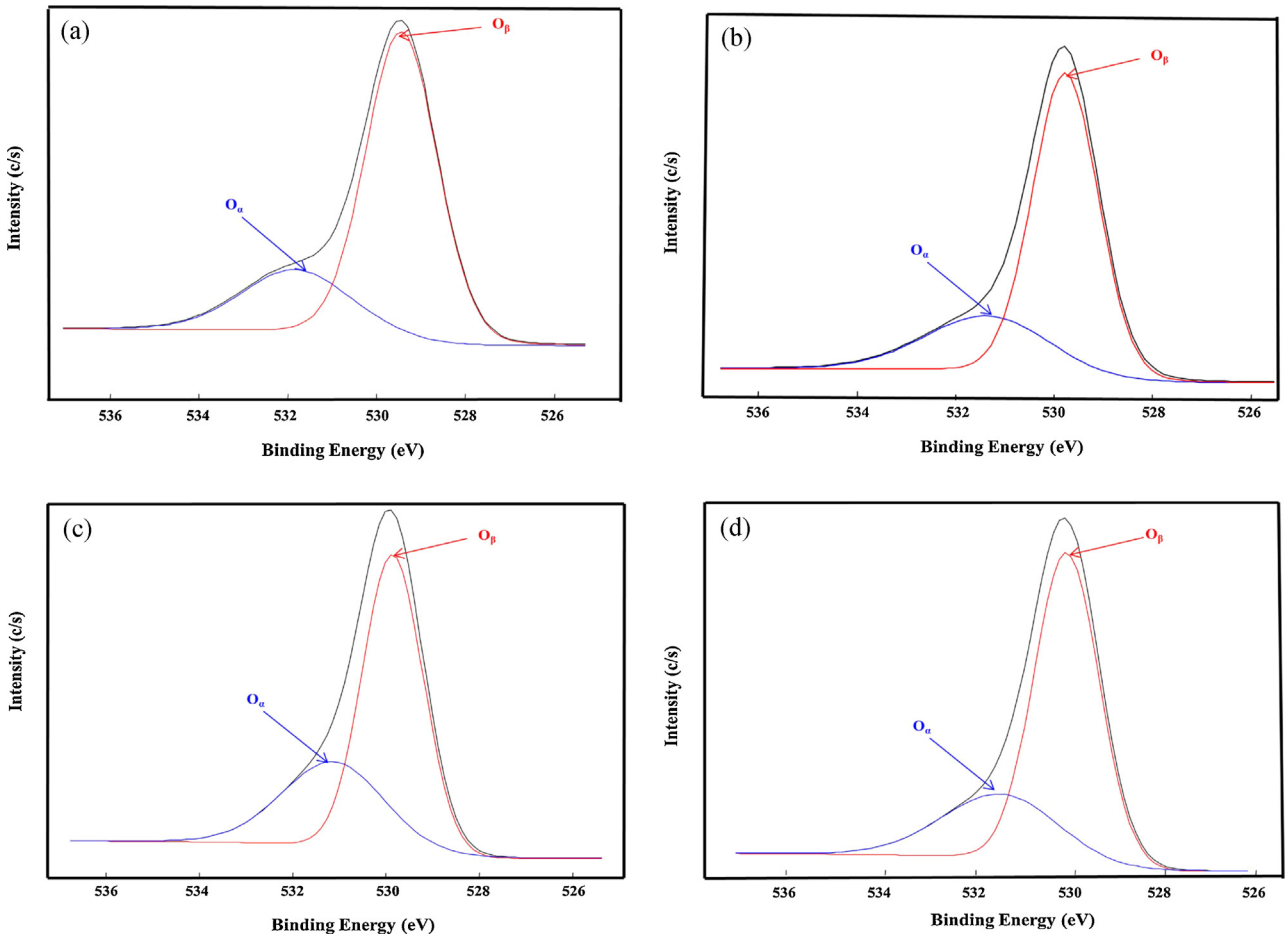

Fig. 12. XPS spectra of O 1s for the catalysts, as-prepared and sulfated at different temperatures: (a) as-prep., (b) S300, (c) S400, and (d) S500.

Table 2
Elemental compositions (weight %) of cerium (Ce), oxygen (O) and sulfur (S) for fresh and sulfated catalysts.

Samples	Ce			O				S
	Ce^{+4}	Ce^{+3}	Ce_{total}	O_α	O_β	O_{total}	Surface (XPS)	Bulk (EDS)
As-prep.	47.1	52.9	0.72	24.7	75.3	76.3	–	–
S300	53.8	46.2	0.26	26.1	73.9	75.8	0.39	0.81
S400	39.9	60.1	0.34	26.9	73.1	67.6	0.76	0.93
S500	34.9	65.1	0.28	27.8	72.2	76.0	1.24	1.12

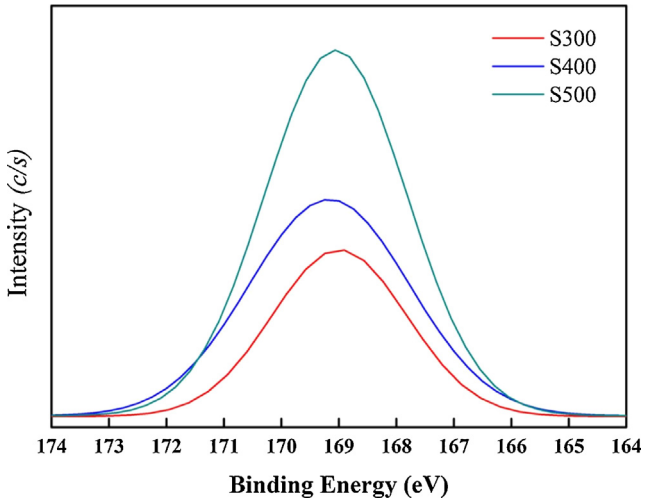

Fig. 13. XPS spectra of S 2p for the catalysts sulfated at different temperatures.

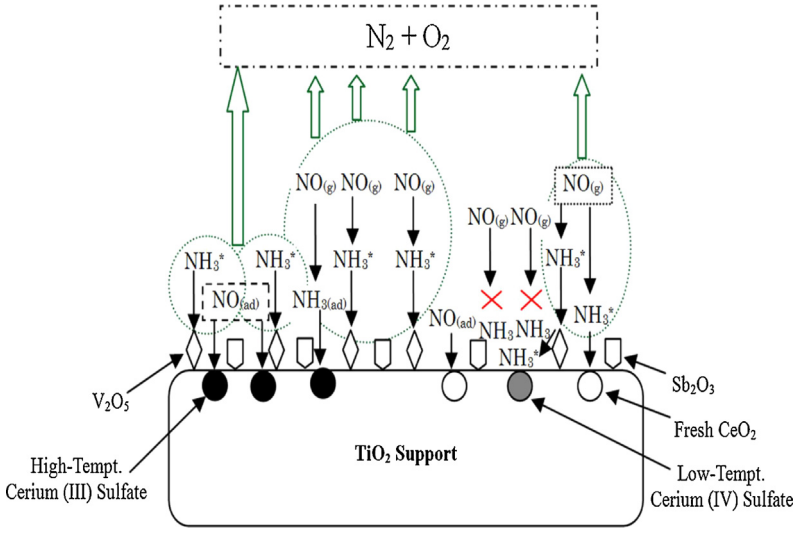

Fig. 14. Plausible reaction mechanism for sulfated catalysts at lower temperature (≈225 °C).

4. Conclusions

10% CeO_2-added, $Sb/V_2O_5/TiO_2$ catalyst was pretreated with SO_2 under oxidizing conditions at 300, 400 and 500 °C, each for 2 h. The increase in surface area after sulfation could be due to amorphous nature of the sulfate species formed. No ceria peak was observed for the sulfated catalysts possibly due to poor CeO_2 crystallinity after sulfation. NH_3 adsorption was increased with increasing sulfation temperature, whereas NO adsorption tendency decreased due to increased acidity of the sulfated catalysts. The difference in NH_3 and NO adsorption patterns suggested difference in nature of the sulfate species formed, which became clear from their mass spectra, H_2-TPR and XPS studies. S500 catalyst showed highest amount of available reducible species. XPS studies could detect increased Ce^{3+} species on the S500 catalyst, in contrast to the S300 sample with higher amount of Ce^{4+} species. Therefore, the high-temperature (500 °C) sulfate species could be referred as Ce(III) sulfate and those formed at low temperature (300 °C) as Ce(IV) sulfate. The activity results proved that the cerium(III) sulfate species formed at 500 °C were more active, as compared to those formed at lower temperatures. Specifically, cerium(IV) sulfates formed at 300 °C were found to be unfavorable for NH_3-SCR of NO_x for prolonged time periods at low temperatures, resulting in poisoning and deactivation of the catalyst.

Acknowledgements

This work was financially supported by 'Future Core Technology' program from KIST. The grant from 'Fundamental R&D Program for the Core Technology of Materials', funded by the Ministry of Knowledge Economy, Republic of Korea is also highly acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2014.01.017.

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